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Timed Diels-Alder Reactions

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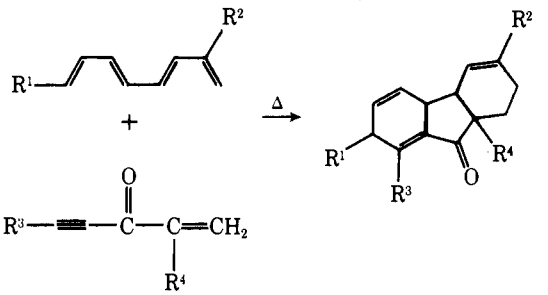
Abstract: In this paper a unique approach to the synthesis of polycyclic ring systems is disclosed. The approach features an intermolecular Diels-Alder reaction followed by an intramolecular Diels-Alder reaction where the regiochemistry of addition is controlled by substituents on the bisdiene and bisdienophile. This methodology has been applied to the synthesis of the fluorenone ring system.

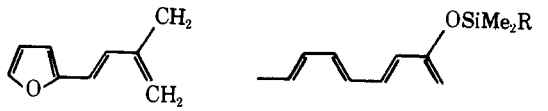
An efficient convergent strategy is vital for the practical synthesis of polycyclic systems. This postulate has motivated the creation of ingenious routes to steroids,[1] vitamins,[2] and alkaloids.[3] We have recently discovered a novel method, the general features of which are depicted below. In this polycy-



cloaddition (termed a "timed Diels-Alder") a tricyclic ring system is formed *regiospecifically* in a *single* reaction. In principle, a number of compounds might be formed. However, one of the diene units in the bisdiene is more reactive than the other unit. The same feature is true for the bisdienophile. Thus, the initial ring is created by cycloaddition of the more reactive diene and dienophile. The second and third rings are formed by the intramolecular cycloaddition of the less reactive diene and dienophile. At present, we have confined our study to the formation of the fluorenone ring system.

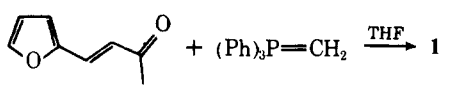
Results and Discussion

Synthesis of Reactants. The bisdienes used in this investigation were compounds **1** and **2**. The preparation of **1** was

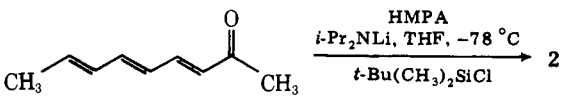


1 **2** (R = CH_3, *t*-Bu)

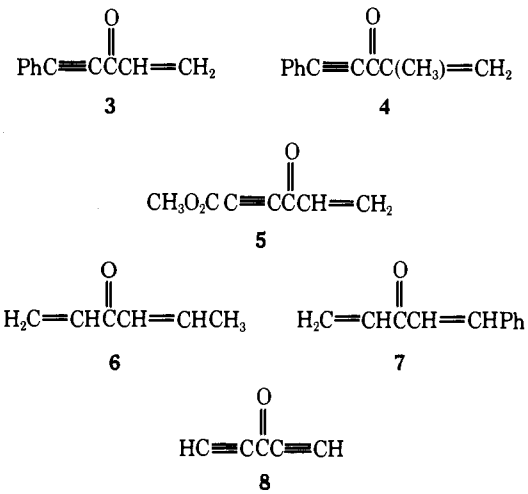
readily accomplished by the use of a Wittig reaction on 4-(2-furyl)-3-buten-2-one.[4] It could be purified by bulb to bulb



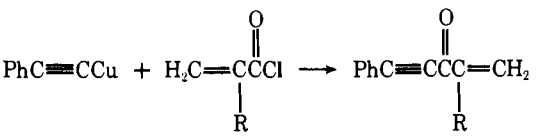
distillation or by filtration through silica gel. Bisdiene **2** could be synthesized by trapping the kinetic anion of 3,5,7-octatrien-2-one[5] with chlorodimethyl-*tert*-butylsilane or chlorotrimethylsilane. Both bisdienes were unstable to prolonged



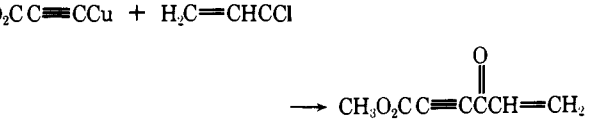
storage but could be stored for days under an inert atmosphere at 0 °C. The array of bisdienophiles employed in this study consisted of enynones **3**, **4**, and **5**, dienones **6** and **7**, and diynone



8. The enynones **3** and **4** were made by the coupling of cuprous



phenylacetylide with the requisite acid chloride according to the method of Normant.[6] Enynone **5** was similarly prepared.



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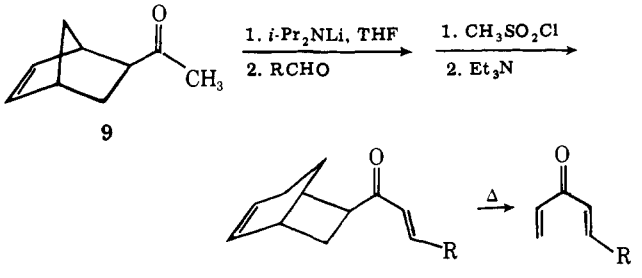
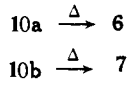
Dienones **6** and **7** were efficiently synthesized from ketone **9** by aldol condensation, dehydration, and a retrograde Diels-Alder reaction. Dehydration could be most effectively ac-

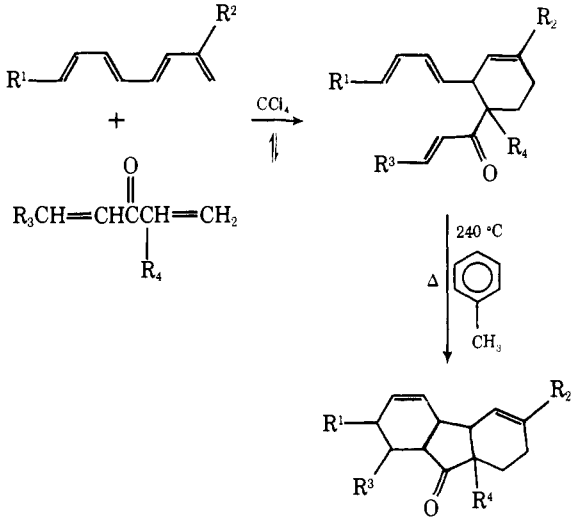


complished by mesylation followed by reaction with triethylamine[7] to form **10a** or **10b**. Compounds **10a** and **10b** were ex-

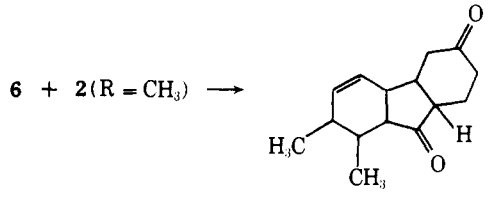


clusively trans enones. These compounds were then subjected to flow pyrolysis conditions (600 °C, 20 mm) to afford dienones **6** and **7**. Diynone **8** had been previously prepared.[8]

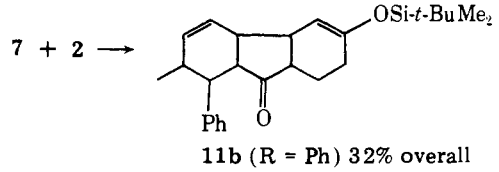
Diels-Alder Reactions. The optimal conditions for the polycycloaddition reaction were found to be the reaction in refluxing CCl_4[9] to form the first cyclohexene ring followed by a sealed tube reaction at elevated temperatures to effect closure to the tricyclic system. No tricyclic product was obtained after



reaction at ambient temperature for 1 week. If the reactants were simply heated at 240 °C, the yield of the desired tricyclic structure was greatly reduced owing to polymer formation. The results with dienones **6** and **7** and bisdiene **2** are illustrated below. The proposed structure of **11a** is supported by infrared



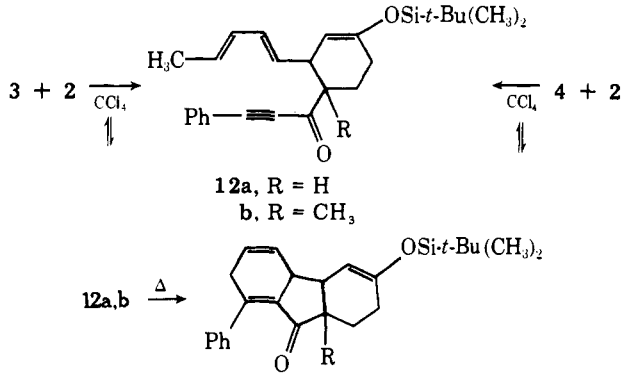
11a (R = CH_3) 35% overall



11b (R = Ph) 32% overall

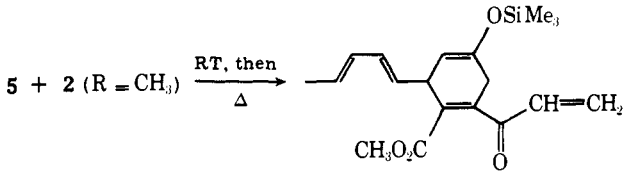
absorptions at 1720 and 1740 cm^{-1}. Similar information (absorption at 1735 cm^{-1}) can be obtained from the spectra for **11b**. Both compounds are homogeneous by thin layer chromatography.

Enynones **3**, **4**, and **5** undergo Diels-Alder reaction with **2** as illustrated below. Cyclohexenes **12a,b** show absorptions



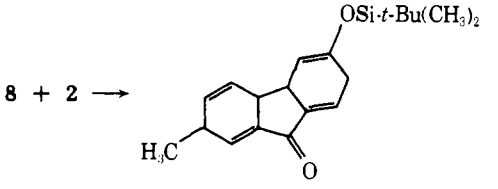
13a, R = H 30% overall
b, R = CH_3 28% overall

corresponding to ynones (2200, 1620 cm^{-1}). The NMR spectra indicate the absence of enone hydrogens. After thermal cyclization, compounds **13a** or **13b** are obtained. The infrared spectra of both **13a** and **13b** lack the intense acetylenic absorption characteristic of **12a** and **12b**. In contrast to the behavior of enynones **3** and **4**, the Diels-Alder reaction of **5** with bisdiene **2** afforded only monoaddition to yield **14**. In this case



14

the orientation was governed by the directing effects of the carbomethoxy group. The Diels-Alder reaction of diynone **8** with **2** presented unexpected difficulty because of the instability of the monocyclic adduct at elevated tmperatures. The optimal conditions for cyclization involved heating the reactants in warm carbon tetrachloride overnight. Adduct **15** could



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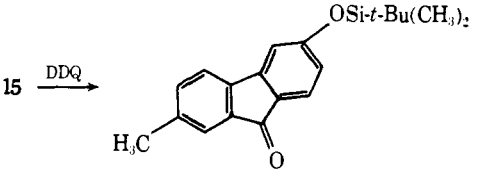
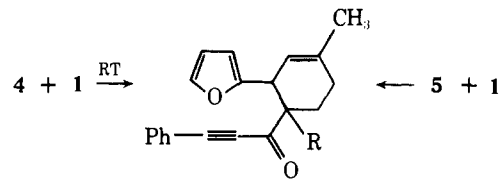
be smoothly dehydrogenated to the fluorenone with DDQ.[10] Compound **16** exhibited the ultraviolet and infrared spectra



16

characteristic of a 3-alkoxyfluorenone. Both high-resolution and low-resolution mass spectroscopy also support the assigned structure.

The Diels-Alder reactions of bisdiene **1** with enynones **4** and **5** proceed *only* to the monocyclic compound. No conditions



17a, R = H
b, R = CH_3

could be found for the cyclization of mono adduct **17a** or **17b**. While this work was in progress, Parker and co-workers[11] published results on simpler systems which support our observations.

From the results presented above, it is clear that a delicate balance between relative reactivity and the directing effects of substituents on the bisdiene is involved for the successful cycloaddition. If one of the diene units in the bisdiene is unreactive or if an unfavorable equilibrium exists between adduct and uncyclized compound, this polycycloaddition concept cannot be used successfully. Another interesting facet of this reaction is the control of stereochemistry. In the cycloaddition between **2** and a dienone six chiral centers are created, whereas between **2** and an enynone only four chiral centers are developed. The assumptions of a concerted cycloaddition and the well-documented preference for endo addition limit the number of possible permutations which can be obtained. An analysis of stereochemistry must begin with a study of the initially formed adduct, since the stereochemistry created in the monocyclic structure might be expected to direct the development of the remaining asymmetric centers.[12] The ^{13}C NMR spectrum of **12a** showed that only one isomer had been formed. In the case of adduct **12b**, the NMR spectrum indicated only one singlet corresponding to the quaternary methyl group. After thermal cycloaddition to the adduct **13a** or **13b**, however, the ^{13}C NMR of purified product indicated that a mixture of stereoisomers had been formed. This mixture could not be separated by column or gas chromatography. Analysis of the ^{13}C spectra of adduct **11b** also indicated that an isomeric mixture had been obtained.

In addition to the rapid formation of the fluorenone skeleton which is present in a variety of natural products such as the gibberelins[14] and antharidiogens,[15] this method is also quite useful for the preparation of substituted fluorenones for which selective synthetic methods are not presently available. We are presently evaluating the utility of this reaction for the synthesis of compounds containing the phenanthrene and anthracene skeleton.

Experimental Section

IR spectra were obtained on a Beckman IR 4250 spectrometer. NMR spectra were recorded using Varian EM-360 and A-60 spectrometers. All chemical shifts are reported in δ relative to tetramethylsilane as an internal standard. An AE1-MS902 mass spectrometer was used for mass spectral data. UV spectra were recorded on a Cary-14 spectrometer. ^{13}C NMR spectra were run on a Joelco FX-90Q spectrometer. The standard is Me_4Si.

Preparation of 4-(2-Furyl)-2-methyl-1,3-butadiene (1). To a suspension of 1.97 g (5.5 mmol) of methyltriphenylphosphonium bromide in THF at −40 °C was added a 1 M THF solution of 5.5 mmol of LDA.[16] The reaction mixture was allowed to slowly warm to 0 °C and stirred at 0 °C until all the salt had dissolved. The reaction mixture was cooled to −40 °C. A THF solution (2 M) of 4-(2-furyl)-3-buten-2-one (0.68 g, 5 mmol) was added dropwise over 2 min. The reaction mixture was allowed to slowly warm to room temperature and stir for 10 h. The reaction mixture was diluted with an equal volume of hexane and filtered through a column of Florisil (25 g) using hexane as the eluent. Concentration of the organic solution yielded 0.56 g (4.18 mmol, 84%) of **1**: NMR (CCl_4) δ 1.94 (br s, 3 H), 5.15 (m, 2 H), 6.20 (m, 1 H), 6.28 (d, 1 H, J = 8 Hz), 6.30 (m, 1 H), 6.88 (d, 1 H, J = 8 Hz), 7.40 (m, 1 H); IR (film) cm^{-1} 3120, 1615, 955, 880; high-resolution mass spectrum $C_9H_{10}O$ requires 134.073 17, measured 134.071 68.

Preparation of 2-(Dimethyl-*tert*-butylsiloxy)-1,3,5,7-nonatetraene (2). To a solution of a 1:1 LDA-HMPA complex[17] (11 mmol) in 15 mL of THF at −78 °C was added a 2 M THF solution of 1.36 g (10 mmol) of 3,5,7-nonatrien-2-one. The reaction mixture was stirred at −78 °C for 20 min. A 2 M THF solution of 1.806 g (12 mmol) of *tert*-butyldimethylsilyl chloride was added and the reaction mixture allowed to stir at room temperature for 3 h. The reaction mixture was poured into 100 mL of hexane and washed with H_2O and brine. The organic solution was dried (Na_2SO_4), filtered, and concentrated in vacuo, yield 2.5 g (100%) of **2**: NMR (CCl_4) δ 0.2 (s, 6 H), 1.02 (s, 9 H), 1.8 (d, 3 H, J = 6 Hz), 4.30 (bs, 2 H), 5.72–6.50 (envelope, 6 H); high-resolution mass spectrum $C_{15}H_{26}OSi$ requires m/e 250.175 30, measured m/e 250.174 92; IR (film) cm^{-1} 3020, 2960, 2940, 2860, 1605, 1250, 980.

General Procedure for Enynones 3, 4, and 5. The copper acetylides were prepared according to the method of Castro.[18] To a stirred suspension of 10 mmol of copper acetylide and 10 mmol of LiI in 20 mL of ether was added 10 mmol of the appropriate acid chloride. The reaction mixture was stirred at room temperature for 2 h. To the reaction mixture was added 5 mL of HMPA. The reaction mixture was allowed to stir at room temperature overnight. It was then poured into 50 mL of hexane and washed with 5 M HCl and brine. The organic solution was dried (Na_2SO_4), filtered, and concentrated. The residue was chromatographed on silica gel using hexane–ether as the solvent.

1-Phenyl-4-penten-1-yn-3-one (3): yield 1.40 g (90%); NMR (CCl_4) δ 6.18 (m, 1 H), 6.54 (m, 2 H), 7.5 (m, 5 H); IR (film) cm^{-1} 2196, 1640, 1603; high-resolution mass spectrum $C_{11}H_8O$ requires 156.057 52, measured 156.0558.

4-Methyl-1-phenyl-4-penten-1-yn-3-one (4): yield 1.45 g (85%); mp 56 °C (recrystallized from hexane); NMR (CCl_4) of 1.97 (br s, 3 H), 6.05 (m, 1 H), 6.54 (m, 1 H), 7.5 (m, 5 H); IR (CCl_4) cm^{-1} 2200, 1645, 1488, 1330, 1080, 990, 935, 860; high-resolution mass spectrum $C_{12}H_{10}O$ requires m/e 170.073 17, measured m/e 170.070 41.

Ethyl 4-Oxo-5-hexen-2-ynoate (5): yield 0.91 g (60%); NMR (CCl_4) 1.38 (t, 3 H, J = 3.8 Hz), 4.36 (q, 2 H, J = 3.8 Hz), 6.25 (m, 1 H), 6.55 (m, 2 H); IR (film) cm^{-1} 2983, 2140, 1720, 1660, 1440, 1420, 985, 783, 750; high-resolution mass spectrum $C_8H_8O_3$ requires m/e 152.047 35, measured m/e 152.045 10.

General Procedure for Monocycloaddition Products. A 0.5 M CCl_4 solution of 2 mmol of the appropriate bisdiene and 2 mmol of the appropriate bisdienophile was refluxed under nitrogen. The progress of the reaction was followed by NMR. When the reaction was judged complete, the reaction mixture was concentrated and the residue chromatographed on silica gel using hexane–ether as the solvent.

1-(2-(1,3-Pentadienyl)-4-*tert*-butyldimethylsilyloxycyclohex-3-enyl)-3-phenylpropyn-1-one (12a): yield 0.45 g (55%); NMR (CCl_4) δ 0.20 (s, 6 H), 1.0 (s, 9 H), 1.78 (d, 3 H, J = 6 Hz), 4.88 (m, 1 H), 5.6–6.2 (envelope, 4 H), 7.55 (m, 5 H); IR (film) cm^{-1} 2980, 2200, 1665; ^{13}C NMR ($CDCl_3$) 17.95, 24.06, 25.69, 28.42, 39.34, 39.47, 54.43, 105.74, 120.18, 128.30, 129.15, 130.58, 131.10, 131.30, 132.99, 133.38, 135.72, 150.55, 189.82.

1-(2-(1,3-Pentadienyl)-1-methyl-4-*tert*-butyldimethylsilyloxycyclohex-3-enyl)-3-phenylpropyn-1-one (12b): yield 0.42 g (50%); NMR (CCl_4) δ 0.20 (s, 6 H), 1.0 (s, 9 H), 1.18 (br s, 3 H), 1.80 (d, 3 H, J = 6 Hz), 4.90 (m, 1 H), 5.60–6.20 (envelope, 4 H), 7.55 (m, 5 H); IR (film) cm^{-1} 2980, 2200, 1660, 1195, 832.

Methyl 6-(1,3-Pentadienyl)-2-(1-oxopropenyl)-4-*tert*-butyldimethylsilyloxy-3,6-dihydrobenzoate (14): yield 0.346 g (50%); NMR (CCl_4) δ 0.20 (s, 9 H), 1.85 (d, 3 H), 6.1–6.6 (acryloyl pattern, 3 H); IR (film) cm^{-1} 3015, 2980, 2910, 1720, 1690, 1260.

2,4a,4b,7-Tetrahydro-7-methyl-3-*tert*-butyldimethylsilyloxy-9*H*-fluoren-9-one (15): yield 0.22 g (34%); NMR (CCl_4) δ 0.20 (s, 6 H), 1.0 (s, 9 H), 4.80 (m, 1 H), 6.30 (m, 2 H), 6.90 (m, 2 H); IR (film) cm^{-1} 2960, 2930, 2860, 1710, 1598, 1465, 1350, 1265, 1215, 930.

1-(2-(2-Furyl)-4-methylcyclohex-3-enyl)-3-phenylpropyn-1-one (17a): yield 0.20 g (35%); NMR (CCl_4) δ 1.74 (br s, 3 H), 5.50 (m, 1 H), 5.95 (m, 1 H), 6.15 (m, 1 H), 7.4 (m, 6 H); IR (film) cm^{-1} 2200, 1720, 1665, 750, 682.

1-(2-(2-Furyl)-1,4-dimethylcyclohex-3-enyl)-3-phenylpropyn-1-one (17b): yield 0.22 g (37%); NMR (CCl_3) δ 1.35 (s, 3 H), 1.77 (br s, 3 H), 5.40 (m, 1 H), 5.95 (m, 1 H), 6.15 (m, 1 H), 7.4 (m, 6 H); IR (film) cm^{-1} 2200, 1665, 1280; high-resolution mass spectrum $C_{21}H_{20}O_2$ requires 204.146 33, measured 304.144 56.

General Procedure for Second Cycloaddition. The appropriate monocycloaddition product was dissolved in enough toluene to make the solution ~0.10 M. The solution was degassed by bubbling argon through for ~5 min. The solution was heated in a sealed tube at 240 °C for 3-5 h. The solution was concentrated and the residue chromatographed on silica gel using ether-hexane as the solvent.

1,2,4a,4b,7,8,8a,9a-Octahydro-7,8-dimethyl-3,9*H*-fluorene-3,9-dione (11a): yield 0.16 g (35% overall); IR (film) 1720, 1745, 1450 cm^{-1}; NMR ($CDCl_3$) δ 1.1-1.35 (m, 6 H), 2.0-3.1 (broad m, 12 H), 5.6-5.9 (bs, 2 H).

1,2,4a,4b,7,8,8a,9a-Octahydro-7-methyl-8-phenyl-3-*tert*-butyldimethylsilyloxy-9*H*-fluoren-9-one (11b): yield 0.26 g (32% overall); NMR (CCl_4) δ 0.20 (s, 6 H), 0.70 (d, 3 H, J = 7 Hz), 1.0 (s, 9 H), 5.05 (m, 1 H), 6.20 (m, 2 H), 7.5 (m, 5 H); IR (film) cm^{-1} 1735, 1648, 1250, 1190, 835, 780; high-resolution mass spectrum $C_{26}H_{36}O_2Si$ requires 408.248 47, measured 408.248 56.

1,2,4a,4b,7,9a-Hexahydro-7-methyl-8-phenyl-3-*tert*-butyldimethylsilyloxy-9*H*-fluoren-9-one (13a): yield 0.24 g (30% overall); NMR (CCl_4) δ 0.2 (s, 6 H), 1.0 (s, 9 H), 5.1 (m, 1 H), 5.85 (m, 1 H), 6.0 (m, 1 H), 7.4 (m, 5 H); IR (film) cm^{-1} 1720, 1660, 1250, 1190, 832; high-resolution mass spectrum $C_{26}H_{34}O_2Si$ requires 406.232 81, measured 406.232 70.

1,2,4a,4b,7,9a-Hexahydro-7,9a-dimethyl-8-phenyl-3-*tert*-butyldimethylsilyloxy-9*H*-fluoren-9-one (13b): yield 0.235 g (28% overall); NMR (CCl_4) δ 0.20 (s, 6 H), 1.0 (s, 9 H), 5.0 (m, 1 H), 5.90 (m, 1 H), 6.05 (m, 1 H), 7.50 (m, 5 H); IR (film) cm^{-1} 1720, 1640, 1460, 1190, 830; high-resolution mass spectrum $C_{27}H_{36}O_2Si$ requires 420.248 46, measured 420.248 38.

7-Methyl-3-*tert*-butyldimethylsilyloxy-9*H*-fluoren-9-one (16). To a stirred solution of 22 mg of **15** in 2 mL of toluene was added 30 mg of DDQ. The reaction mixture was refluxed for 24 h. The solution was diluted with ether, filtered, and concentrated: yield 0.21 g (100%); NMR ($CDCl_3$) δ 0.28 (s, 6 H), 1.02 (s, 9 H), 2.36 (s, 3 H), 7.45 (m, 6 H); IR ($CHCl_3$) cm^{-1} 1700, 1600, 1255, 1215, 833, 791; high-resolution mass spectrum $C_{20}H_{24}O_2Si$ requires 324.154 56, measured 324.151 14; UV (MeOH) 256, 278 nm.

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Production of a Fluorescent Conjugate Acid of 8-Methoxypsoralen and an Unusual Mechanism for Its Nonradiative Decay

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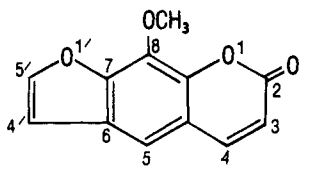
Abstract: The protonation constant (pK_{BH^+}) of 8-methoxypsoralen was determined from measurements of its absorption in various concentrations of sulfuric and perchloric acids using Hammett acidity functions. Proton nuclear magnetic resonance spectra of highly acidic solutions indicated protonation of the exocyclic oxygen atom. With D_2SO_4, proton exchange with the furan side of the molecule (4′,5′ positions) was observed. The intensity of fluorescence of the conjugated acid increases markedly with increasing acid concentration in solutions where absorption measurements indicate that protonation is nearly complete. This unexpected behavior is discussed and a mechanism is proposed.

Introduction

Initially, our interest in 8-methoxypsoralen (8-MOP) was sparked by the use of that compound in a novel and experimental treatment of psoriasis. In the treatment, the compound is ingested or applied topically, and after a suitable time interval the patient is irradiated with ultraviolet radiation of wavelengths longer than 300 nm. While the mechanism by which the photochemotherapy alleviates the symptoms is not fully understood, it is believed to involve the photoaddition of 8-MOP to epidermal DNA.



8-methoxypsoralen (8-MOP)

We were examining the fluorescence quenching of 8-MOP with various quenchers with the intent of using this data to help elucidate the distribution of the compound in tissue samples. One of the first quenchers we studied was H^+, provided by different strong acids. The quenching followed Stern-Volmer kinetics[1] but, much to our surprise, we observed no new fluorescence, attributable to the conjugate acid of 8-MOP. We had reasoned by analogy to the related compounds, the 7-amino-

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